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Sustainable cyclic carbonate production, utilising carbon dioxide and azolate ionic liquids

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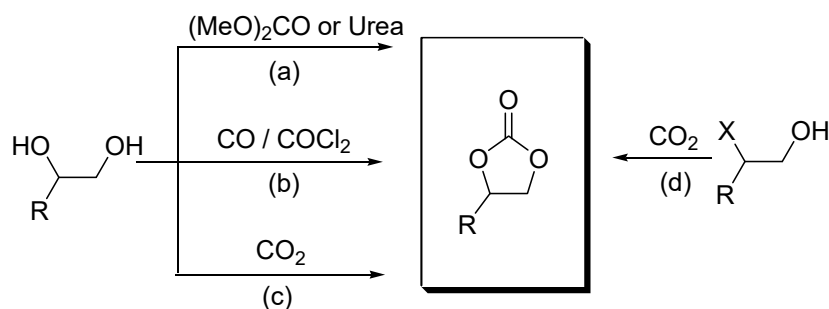
Abstract:

An efficient protocol is described for producing cyclic carbonates in good to excellent yields under moderate reaction conditions (100.0 °C, 1.0 MPa) by treating epoxides with carbon dioxide, promoted by a series of azolate ionic liquids, which are effective recyclable metal-free and halide-free catalysts.

Keywords: Green chemistry, azolate ionic liquids, recyclable catalysts, epoxides, cyclic carbonates.

INTRODUCTION

Carbon dioxide is a greenhouse gas thought to be involved in global warming and climate change.^{1,2} Nevertheless, it offers a virtually inexhaustible, inexpensive, non-flammable and readily available C1 feedstock for organochemical processes.³⁻⁷ The direct conversion of CO₂ to five- or six-membered cyclic carbonates⁸⁻¹⁰ is one of the most promising strategies for producing highly desirable solvents for electrolytes in Li-ion rechargeable batteries.^{11,12} Cyclic carbonates are also utilised as monomers in polymerisation reactions,^{13,14} as intermediates in the synthesis of fine chemicals⁷ and as high boiling aprotic polar solvents.¹⁵⁻¹⁷ There have been many varied reports of synthetic routes to yield cyclic carbonates, and the most important of these are summarised in Scheme 1. In addition, Lewis acidic catalysts including SnCl₄¹⁸, cobalt porphyrin¹⁹ and chromium / zinc / aluminum salen^{20, 21} have also been reported to catalyze this cycloaddition reaction. However, most of these catalyst systems need bases or tetraalkylammonium halides as co-catalysts; and in some cases, either the use of expensive reagents or harsh reaction conditions were required for an efficient reaction.²²⁻³³



| Entry | Substrate | “CO” Source | Catalyst system | Conditions | Yield / % | Ref |
|-------|-------------|-----------------------|--|--|-----------|-------|
| 1 | 1,2-diols | Urea | FeBr ₂ | 150.0 °C, 18.0 h, 1,4-dioxane | 92.0 | 22 |
| 2 | 1,2-diols | (MeO) ₂ CO | NHC ^a | 74.0 °C, 6.0 h | 58.0 | 23 |
| 3 | 1,2-diols | CO | Pd/C, KI, O ₂ , Na[O ₂ CMe] | 100.0 °C, 3.0 h, 1.5 MPa, MeOCH ₂ CH ₂ OMe | 91.0 | 24-26 |
| 4 | 1,2-diols | CO ₂ | NHC ^a /Base/RX | 90.0 °C, 24.0 h, 0.1 MPa | 81.0 | 28 |
| 5 | Haloalcohol | CO ₂ | Basic ionic liquids | 25.0 °C, 14.0 h, 1.0 MPa | 90.0 | 29 |
| 6 | Haloalcohol | CO ₂ | Cs ₂ CO ₃ | 40.0 °C, DMF, 0.1 MPa | 75.0 | 30 |

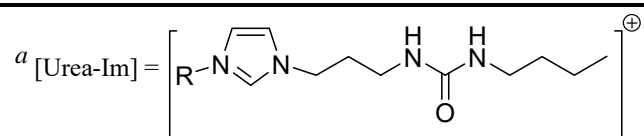
^a NHC= *N*-heterocyclic carbene

Scheme 1. Synthesis of cyclic carbonates from organic precursors.

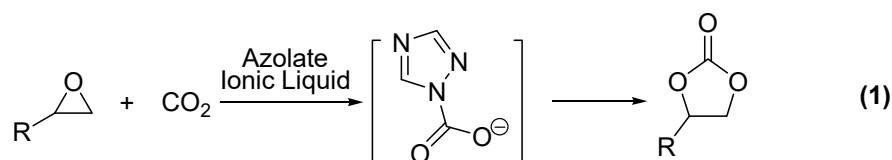
Ionic liquids³⁴ have been used for the synthesis of a myriad of organic chemicals.³⁵ Of specific interest here, there have been number of attempts to use ionic liquids to make cyclic carbonates.³⁶⁻⁴² Some key processes, to date, using homogenous ionic liquid systems are summarised in Table 1. It is noteworthy, that there have also been a number of solid-supported ionic liquid systems⁴¹⁻⁴⁶ employed for producing cyclic carbonates. Though they produce high yields of products, these systems also contain undesirable halides and/or metals.

Table 1. Halide ionic liquids catalysed cycloaddition reactions of epoxides and CO₂.

| Entry | Epoxide | IL | Conditions | Yield % | ref |
|-------|-----------------|---|--------------------------|---------|-----|
| 1 | Styrene oxide | [ArPPh ₃]Br | 60.0 °C, 24.0 h, 0.1 MPa | 91.0 | 36 |
| 2 | Propylene oxide | [(mim) ₂ Zn]Br ₂ | 120.0 °C, 4.0 h, 0.5 MPa | 78.0 | 37 |
| 3 | Propylene oxide | [Urea-Im]I ^a | 130.0 °C, 3.0 h, 1.0 MPa | 97.0 | 38 |
| 4 | Propylene oxide | [(HOCH ₂ CH ₂) ₃ NH]I | 110.0 °C, 6.0 h, 2.0 MPa | 91.0 | 39 |
| 5 | Epichlorohydrin | [bim-ArOH]Br | 120.0 °C, 1.0 h, 1.0 MPa | 90.0 | 40 |



The work described in this paper, utilises ionic liquids with azolate anions, which in previous literature reports refer to as *superbasic ionic liquids*.⁴⁷ Even though they are more basic than common trialkylamines, the pK_a values of their conjugate acids would not warrant them to qualify as superbasic substances.⁴⁸⁻⁵⁰ Nevertheless, their associated anions possess sufficiently high nucleophilicity to attach weakly electrophilic CO₂, enabling them to be used in CO₂ gas capture and catalysis.^{47, 51-55} In this paper, we refer to them as *azolate ionic liquids (or salts)*.



The key step (see equation 1) in this reaction is the formation of a reactive carbamate intermediate by nucleophilic addition of the azolate anion to CO₂. This carbamate intermediate

also has been shown to react with other substrates, including propargylic alcohols, 2-aminobenzonitriles, 1,2-phenylenediamines, and 2-aminothiophenol, thereby producing α -alkylidene cyclic carbonates,⁵³ or α -hydroxy ketones,⁵⁴ quinazoline-2,4(1H,3H)-diones,⁵⁵ benzimidazolones,⁵⁵ and benzothiazoline,⁵⁵ respectively.

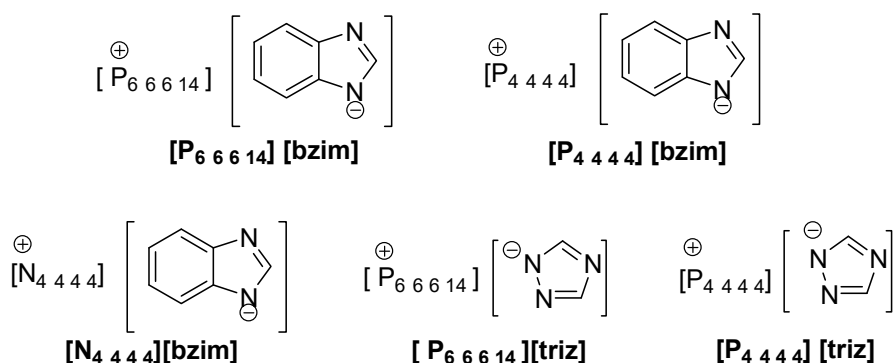


Figure 1. The azolate ionic liquids (or salts) used in this work.

Herein, we report a protocol involving metal- and halide-free azolate ionic liquid system for promoting the cycloaddition of CO₂ to epoxides to generate cyclic carbonates. These ionic liquids (or salts) contain benzimidazolate (bzim) or triazolate (triz) anions and trihexyltetradecylphosphonium (P₆₆₆₁₄), tetrabutylphosphonium (P₄₄₄₄) and tetrabutylammonium (N₄₄₄₄) cations (See Figure 1).

EXPERIMENTAL SECTION

Materials. Benzimidazole (98.0%), 1,2,4-triazole (98.0%), tetrabutylammonium hydroxide (10.0% in methanol), propylene oxide (99.0%), styrene oxide (99.0%), 1,2-epoxyhexane (99.0%), 1,2-epoxypentane (99.0%), 1,2-epoxidodecane (99.0%), 1,2-epoxyoctane (99.0%) and cyclohexene oxide (99.0%) were purchased from Sigma-Aldrich and TCI. [P₆₆₆₁₄]Cl and [P₄₄₄₄]Cl were donated from Solvay-Cytec (98.0%). Gaseous carbon dioxide (99.9 %) was

obtained from BOC. Amberlite IRN-78 ion exchange resin was purchased from Alfa Aesar. All of the materials were used without further purification.

Instruments. ^1H and ^{13}C -NMR spectra were all recorded on a Bruker Ultrashield 400 plus spectrometer at 25.0 °C using dimethyl sulfoxide ($\text{dms}\text{-}d_6$) or Chloroform (CDCl_3) as solvent. ESMS-mass spectroscopy measurements were carried out on a Waters LCT Premier instrument with an Advion TriVersa NanoMate injection system (cone voltage 50 V, source 120.0 °C). Thermogravimetric analyses (TGA) were performed using a TGA/DSC thermogravimetric analyser from Mettler-Toledo, Inc. The samples were measured in alumina crucibles, at a heating rate of 5 K min^{-1} under a dinitrogen atmosphere. The onset of the weight loss in each thermogram was used as a measure of the decomposition temperature (the point at 5.0 wt% loss of the sample).

Preparation of ionic liquids.^{57, 58} In a typical reaction, $[\text{P}_{4444}]\text{Cl}$ (19.9 g, 67.5 mmol) was dissolved in absolute ethanol (25.0 cm^3) and passed through a column packed with at least three equivalents (in terms of the number of OH-exchange groups) of anion exchange resin (Amberlite IRN-78, OH-form, which had been prewashed with absolute ethanol to wet sufficiently and remove any air from the resin). The eluent was passed through the same column a further two times and then passed through a fresh column once more. The resultant ethanolic solution of $[\text{P}_{4444}][\text{OH}]$ was tested for the absence of remaining halide ions, using standard acidification and treatment with silver(I) nitrate. The amount of $[\text{P}_{4444}][\text{OH}]$ in its ethanol solution was then determined by ^1H NMR. The necessary amount of benzimidazole (7.8 g, 66.1 mmol) was added into the solution and stirred for 24 h at room temperature. Solvent was removed *in vacuo* and the product was dried for at least 24 h under high vacuum ($\sim 10^{-2}$ bar) at 60.0 °C, yielding the $[\text{P}_{4444}][\text{bzim}]$ as a pale yellow viscous liquid. The other ionic liquids, $[\text{P}_{66614}][\text{bzim}]$ ⁵⁶,

[P_{6 6 6 14}][triz]⁵¹ and [P_{4 4 4 4}][triz]⁵⁴ were prepared by an analogous route. [N_{4 4 4 4}][bzim] was prepared as a white solid by mixing equimolar quantities of tetrabutylammonium hydroxide (10.0% in methanol) and benzimidazole.

General experimental procedure for the cycloaddition reaction of CO₂ and epoxide. All the reactions were carried out in a stainless-steel autoclave (16.0 cm³) equipped with an automatic stirrer (600 rpm) and temperature control system. The selected epoxide (5.0 mmol) and ionic liquid (0.25 mmol) were added into the autoclave successively. CO₂ (1.0 MPa) was charged in the reactor at ambient temperature. The reaction was carried out in the range 25-100 °C under autogenous conditions, for the appropriate time (up to 24 h) with continuous stirring. The autoclave was cooled to room temperature and then the excess of pressure was released, the product was analysed by ¹H NMR spectroscopy.

The detailed results of the reaction between propylene oxide and CO₂ are reported in Table 2, which led to the establishment of optimal conditions. The reactions of other epoxides were studied under these conditions, and these results are detailed in Table 3.

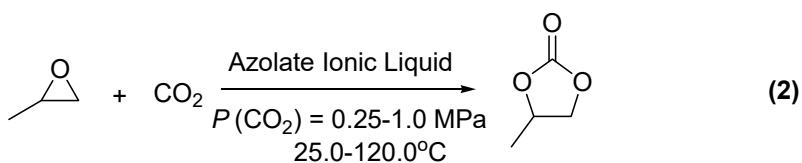
RESULTS AND DISCUSSION

Preparation of ionic liquids

Typically, tetraalkylphosphonium chloride was added to an excess of OH-anion exchange resin, to produce aqueous tetraalkylphosphonium hydroxide solutions, which were then neutralized by the addition of stoichiometric amounts of either a diazole or triazole.⁵⁶⁻⁵⁸ ¹H and ¹³C NMR spectroscopy established both the purity and stoichiometry of the product ionic liquids, and the presence of anions and cations was confirmed by high resolution mass spectrometry. The characteristics of the prepared ionic liquids compared well with earlier literature reports.⁵⁶⁻⁵⁸ All

the products were viscous pale yellow liquids, except [N_{4 4 4 4}][bzim], which was a white powder, and [P_{4 4 4 4}][bzim], which was an immobile glass.

Reaction of propylene oxide with CO₂ The reaction of propylene oxide with carbon dioxide was studied, in detail, under a wide variety of conditions, *viz* temperature, pressure, mol % of ionic liquids and reaction time (see Figure 2, 3 and Table 2). Under all conditions, only a single reaction product, propylene carbonate, was identified, as shown in Equation 2.



A series of experiments were performed in order to find the optimal conditions for the reaction above and then, these conditions were later used to study the reactions of a range of other epoxides (see Table 3).

In specific detail, when the reaction was conducted under ambient conditions using [P_{6 6 6 14}][bzim], only trace amounts of propylene carbonate were observed by NMR spectroscopy (Table 2, entry 2). When the reaction was carried out at 80.0 °C and 1.0 MPa CO₂ pressure, the product yield was elevated to 74.0% (Table 2, entry 3). In a blank experiment, no product was observed in the absence of azolate ionic liquids (Table 2, entry 1). For comparison, the other ionic liquids, including [P_{4 4 4 4}][bzim], [N_{4 4 4 4}][bzim], [P_{6 6 6 14}][triz], and [P_{4 4 4 4}][triz] were examined for this reaction, as well. The results indicated that [P_{4 4 4 4}][bzim] and [N_{4 4 4 4}][bzim] showed the highest reactivity compared with [P_{6 6 6 14}][bzim] (Table 2, entries 3, 4, 5). While [P_{4 4 4 4}][triz] exhibited lower activity than [P_{4 4 4 4}][bzim] (Table 2, entries 4, 7). The significant differences in the chemical structure of these azolate ionic liquids leading to different basicities of the associated anions (pK_a of benzimidazole = 16.4,⁵⁴ pK_a of triazole = 13.9^{51,54}) could be mainly responsible for their capricious catalytic performances. In a previous report,⁵⁶ the azolate ionic liquids with the same anion, [bzim], displayed the highest CO₂ uptake ability due to its high nucleophilicities, which is in accord with its basicity. [P_{4 4 4 4}][bzim] and [P_{6 6 6 14}][bzim], with the same [bzim] anion, the catalytic activity was decreased with increasing

the hydrocarbon chain length of cations (Table 2, entries 3, 4). The same trend was observed in [P₄₄₄₄][triz] and [P₆₆₆₁₄][triz] (Table 2, entries 6, 7), which may be ascribed to the strong interactions between their anions and cations inducing changes in nucleophilicities of anions. The nucleophilicities are seen to be in accord with their basicities. The role of ionic liquid, in here is to activate CO₂ through nucleophilic addition to the anion whilst the organic cation may help solubilization of substrates.

In all cases, the selectivity was > 99.0 %, no by-products were found in ¹H NMR spectroscopy, within its detectable limits, except propylene carbonate, with conversion to propylene carbonate varying between 14.0 and 98.0 %. The best conversion rates were obtained with the most basic anion, benzimidazolate, and at highest temperatures (see Figure 2A). Notably, the yield of propylene carbonate increased dramatically with increasing temperatures. The increase of reaction temperature from 60.0 to 90.0 °C, not only shorten the reaction time but also improve the conversion to cyclic carbonate greatly (Table 2, entries 11-15). On increasing the reaction temperature to 100.0 °C, 93 % conversion was achieved within 2h (entry 16).

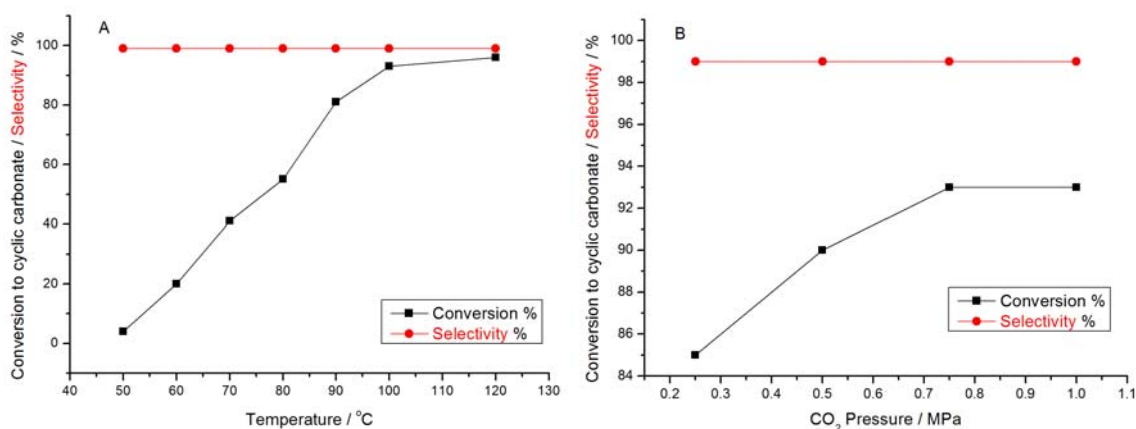


Figure 2. Effect of (A) reaction temperature and (B) CO₂ pressure on the yield of propylene carbonate using [P₄₄₄₄][bzim] ionic liquid. The red lines correspond to selectivity. Reaction conditions are given in Table 2. The errors associated with measuring (i) temperature was ± 0.1 °C; (ii) pressure was ± 0.02 MPa; (iii) NMR spectrometric integrals were ± 2 %

Although higher pressures favored good conversions (see Figure 2B), the yield was not overly sensitive to the CO₂ pressure. The propylene carbonate conversion increased smoothly as the CO₂ pressure increased from 0.25 to 0.75 MPa, while the CO₂ pressure had little effect on propylene carbonate conversion from 0.75 to 1.0 MPa. This indicates that there is a optimum CO₂ pressure influencing the efficiency of the reaction.

Table 2. Conversion of propylene oxide and CO₂ into the corresponding propylene carbonate by azolate ionic liquids^a.

| Entry | Ionic Liquid | Amount of IL/ mol% | <i>T</i> / °C | Time / h | Conversion to cyclic carbonate / % ^b |
|-------|--------------------------------|--------------------|---------------|----------|---|
| 1 | - | - | 80.0 | 5.0 | - |
| 2 | [P _{6 6 6 14}][bzim] | 5.0 | 25.0 | 24.0 | trace |
| 3 | [P _{6 6 6 14}][bzim] | 5.0 | 80.0 | 5.0 | 74.0 |
| 4 | [P _{4 4 4 4}][bzim] | 5.0 | 80.0 | 5.0 | 94.0 |
| 5 | [N _{4 4 4 4}][bzim] | 5.0 | 80.0 | 5.0 | 80.0 |
| 6 | [P _{6 6 6 14}][triz] | 5.0 | 80.0 | 5.0 | 70.0 |
| 7 | [P _{4 4 4 4}][triz] | 5.0 | 80.0 | 5.0 | 75.0 |
| 8 | [P _{4 4 4 4}][bzim] | 5.0 | 40.0 | 24.0 | 14.0 |
| 9 | [P _{4 4 4 4}][bzim] | 5.0 | 50.0 | 24.0 | 54.0 |
| 10 | [P _{4 4 4 4}][bzim] | 5.0 | 50.0 | 3.0 | 4.0 |
| 11 | [P _{4 4 4 4}][bzim] | 5.0 | 60.0 | 24.0 | 62.0 |
| 12 | [P _{4 4 4 4}][bzim] | 5.0 | 60.0 | 3.0 | 20.0 |
| 13 | [P _{4 4 4 4}][bzim] | 5.0 | 70.0 | 3.0 | 41.0 |
| 14 | [P _{4 4 4 4}][bzim] | 5.0 | 80.0 | 3.0 | 55.0 |
| 15 | [P _{4 4 4 4}][bzim] | 5.0 | 90.0 | 3.0 | 81.0 |
| 16 | [P _{4 4 4 4}][bzim] | 5.0 | 100.0 | 2.0 | 93.0 |
| 17 | [P _{4 4 4 4}][bzim] | 5.0 | 120.0 | 2.0 | 96.0 |
| 18 | [P _{4 4 4 4}][bzim] | 1.0 | 100.0 | 3.0 | 57.0 |

| | | | | | |
|----|-------------------------------|------|-------|-----|------|
| 19 | [P _{4 4 4 4}][bzim] | 3.0 | 100.0 | 2.0 | 85.0 |
| 20 | [P _{4 4 4 4}][bzim] | 7.0 | 100.0 | 2.0 | 97.0 |
| 21 | [P _{4 4 4 4}][bzim] | 10.0 | 100.0 | 2.0 | 98.0 |

^a Reaction conditions: Propylene epoxide: 5.0 mmol, IL mol %: with respect to epoxide, stainless-steel autoclave (16.0 cm³), initial CO₂ pressure: 1.0 MPa; ^b Conversion to cyclic carbonate was determined by ¹H NMR spectroscopy. The errors associated with measuring (i) temperature was ± 0.1 °C; (ii) pressure was ± 0.02 MPa; (iii) NMR spectrometric integrals were ± 2 %

Since these reactions were best performed at elevated temperatures (80.0-100.0 °C), the thermal stability of azolate ionic liquids was assessed by TGA. The decomposition temperatures of the two triazolate ionic liquids ([P_{6 6 6 14}][triz], 245.0 °C; [P_{4 4 4 4}][triz], 241.0 °C) were below those of their benzimidazolate analogues ([P_{6 6 6 14}][bzim], 289.0 °C⁵⁶; [P_{4 4 4 4}][bzim], 317.0 °C^{57,58}). However, the tetrabutylammonium salt, [N_{4 4 4 4}][bzim], decomposed around 170.0 °C lower than its phosphonium analogue, indicative of the well-known base-initiated Hoffmann elimination.⁵⁹⁻⁶¹ Thus, for reactions at elevated temperatures, tetraalkylammonium salts should be avoided.

Finally, the effect of the mole ratio of epoxide: ionic liquid was studied. Demonstrably, the ionic liquid performs the role of a basic catalyst, as the epoxide is in significant excess. The almost quantitative conversion of propylene epoxide with a [P_{4 4 4 4}][bzim] loading of 7.0% (Table 2, entry 20) decreased to 57% when the concentration of [P_{4 4 4 4}][bzim] was 1.0% (Table 2, entry 18). The conversion to propylene carbonate did not increase with further increase in the catalyst loading from 7.0% to 10.0% (entries 20, 21). This indicates requirement of an optimum catalyst loading for efficient reaction. From data in Table 2 and Figure 3, it can clearly be seen that increasing the amount of ionic liquid increases the yield of product when other variables are kept constant. The yield of the cyclic carbonate levels out at 7.0-10.0 mol %, and even at 5.0 mol% the yield is only marginally reduced.

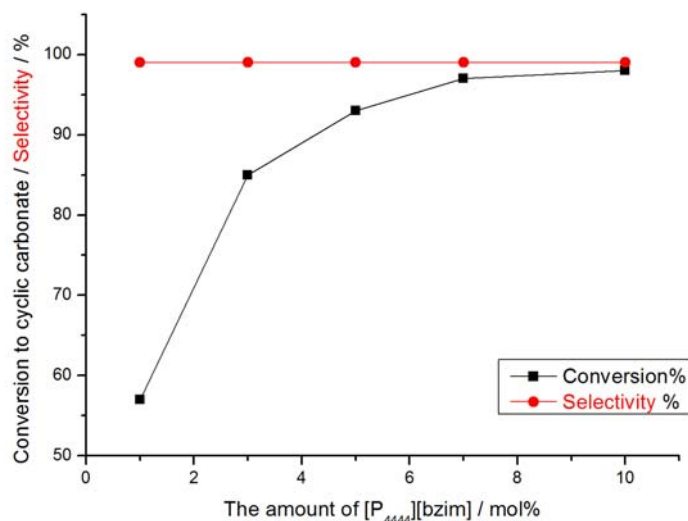


Figure 3. Effect of the amount of [P₄₄₄₄][bzim] on the conversion to propylene carbonate.


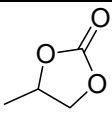
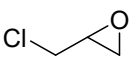
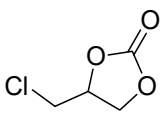
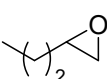
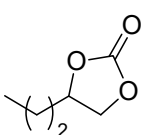
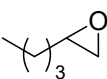
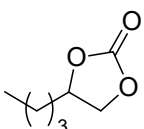
Moreover, not only minimising the quantity of catalyst is important, but also the catalyst needs to be recyclable. Recycling experiments were carried out under the optimum reaction conditions (100.0 °C, 2.0 h, 1.0 MPa). After vacuum removal of propylene carbonate, the recovered ionic liquid, [P₄₄₄₄][bzim], was reused for a further cycle under the same reaction conditions. After four cycles, only a slight lowering of conversion to cyclic carbonate (*ca.* 10.0 %) was observed (See ESI).

The optimal conditions were found to be 100.0 °C, 1.0 MPa CO₂ pressure, 2.0 h and with [P₄₄₄₄][bzim] (5.0 mol %), and these conditions were later used to study the reactions of a range of other epoxides (see Table 3).

Reaction of other epoxides with CO₂ Under the optimal reaction conditions (100.0 °C, P_{CO_2} = 1.0 MPa, 5.0 mol % [P₄₄₄₄][bzim], solvent-free), a range of different epoxides were investigated (Table 3). Remarkably, given the diversity of the precursors, conversion greater than 70.0 % were observed in all cases, with most of the products obtained in greater than 90.0 %.

Even though the yields of cyclic carbonates obtained using other methodologies (see Table 1; alternative reaction conditions and catalysts)³⁶⁻⁴⁶ are comparable to the yields obtained in this work, the catalyst system that is employed here is devoid of metal salts or halides. The novel route reported here is significantly greener and more sustainable than any of the literature alternatives. In particular, the system can be recycled and offers facile product separation. It was noteworthy that, even with a sterically hindered, disubstituted symmetrical substrate such as cyclohexene oxide (Table 3, entry 7), the reaction could still proceed well, giving a reasonable conversion to the corresponding cyclic carbonate. Furthermore, epichlorohydrin (Table 3, entry 2) which carries an additional electrophilic centre also furnished a single product, *viz* cyclic carbonate, emphasising the superior selectivity.

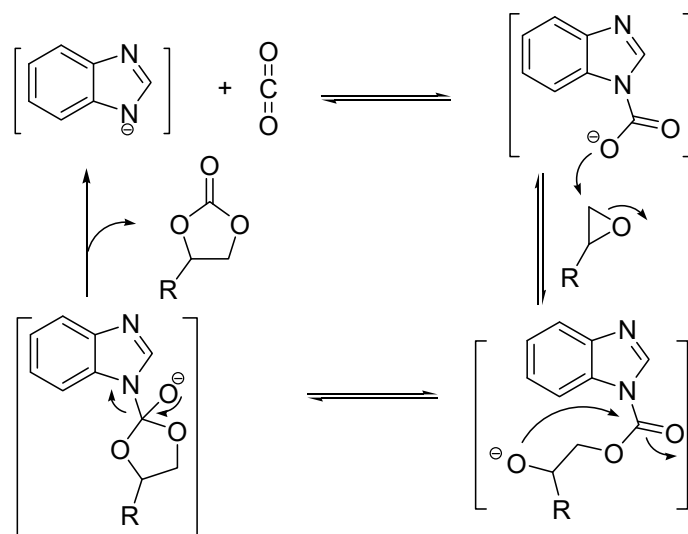
Table 3. Formation of cyclic carbonates from diverse epoxides and CO₂ in the presence of ionic liquid [P₄₄₄₄][bzim]^a

| Entry | Substrate | Product | Time / h | Conversion to cyclic carbonate / % ^b | Ref |
|-------|---|---|----------|---|-----|
| 1 |  |  | 2.0 | 90.3 ^c | 19 |
| 2 |  |  | 3.0 | 88.4 | 19 |
| 3 |  |  | 3.0 | 90.2 | 18 |
| 4 |  |  | 3.0 | 95.4 | 62 |

| | | | | | |
|---|--|--|-----|------|----|
| 5 | | | 3.0 | 89.1 | 63 |
| 6 | | | 4.0 | 88.3 | 19 |
| 7 | | | 3.0 | 71.2 | 18 |
| 8 | | | 3.5 | 90.4 | 19 |

^a Reaction conditions: Epoxide (5.0 mmol), [P₄₄₄₄][bzim] (0.25 mmol, 93.8 mg), CO₂ (1.0 MPa) at 100.0 °C. ^b Isolated yield. ^c Conversion to cyclic carbonate was determined by ¹H-NMR spectroscopy. The errors associated with measuring (i) temperature was ± 0.1 °C; (ii) pressure was ± 0.02 MPa; (iii) NMR spectrometric integrals were ± 2 %

Postulated reaction mechanism. Based on the above data, a plausible mechanism for the reaction of epoxides with carbon dioxide, in the presence of basic ionic liquids, is proposed in Scheme 2. The first step in the mechanism would involve activation of carbon dioxide *via* nucleophilic attack of the azolate anion, producing an anionic carbamate intermediate. The oxygen of the carbamate group is electron rich, and undergoes a nucleophilic attack on the epoxide, causing it to ring-open. This is followed by an intramolecular cyclisation to produce a cyclic carbonate, whilst regenerating the original azolate anion. Alternatively, the azolate anion might attack the epoxide producing an oxo-nucleophile which then further reacts with carbon dioxide to yield the same final product. However, as there is no significant reaction observed between the azolate anion and the epoxide in the absence of CO₂, this alternative mechanism would appear to be less likely.



Scheme 2. A plausible mechanism for cyclic carbonate formation catalysed by $[\text{P}_{4444}][\text{bzim}]$. For simplicity, the spectator cation $[\text{P}_{4444}]^+$ is omitted.

CONCLUSION

In conclusion, several azolate ionic liquids were synthesised and tested as promoters in the cycloaddition reaction of CO_2 and epoxides. Using this protocol, a wide range of epoxide substrates, bearing alkyl, phenyl and halide groups, could be converted to the corresponding cyclic carbonates in good to excellent yields. The catalytic activity of the azolate ionic liquids is influenced significantly by the basicities of the anion, whereas the cation has largely a spectator role. Moreover, the ionic liquid could be recycled for several runs with little loss of activity. This suggests that treating epoxides with carbon dioxide in the presence of, in particular, tetrabutylphosphonium benzimidazolate, represents a new generic approach to the synthesis of cyclic carbonates. Moreover, the procedure not only utilises CO_2 , but is also highly efficient, green, halide- and metal- free, recyclable, and catalytic.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

The synthesis of [N₄₄₄₄][bzim] and the characterisation of azolate ionic liquids, ¹H NMR, ¹³C NMR, MS, TGA, DSC are listed.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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REFERENCES

(1) Huppert, H. Carbon capture and storage in Europe EASAC Policy Report 20, German National Academy of Sciences, Leopoldina, 2013.

(2) Hoeven, M. van der; Kobayashi, Y. and Diercks, R. Technology roadmap: energy and GHG reductions in the chemical industry *via* catalytic processes, International Energy Agency, Paris, 2013, p. 56.; International Council of Chemical Associations (ICCA), Innovations for Greenhouse Gas Reductions: A life cycle quantification of carbon abatement solutions enabled by the chemical industry, 2009, p. 108.

(3) Aresta, M.; Dibenedetto, A. and Angelini, A. Catalysis for the valorization of exhaust carbon: from CO₂ to chemicals, materials, and fuels. Technological use of CO₂. *Chem. Rev.*, 2014, **114**, 1709-1742.

(4) Aresta, M. and Van Eldik, R.; *Advances in inorganic chemistry* 2014, **66**, CO₂ Chemistry, 2014, Elsevier Inc. All rights reserved.

(5) Tlilu, A.; Blondiaux, E.; Frogneux X. and Cantat, T. Reductive functionalization of CO₂ with amines: an entry to formamide, formamidine and methylamine derivatives. *Green Chem.*, 2015, **17**, 157-168. (DOI:10.1039/C4GC01614A)

(6) Hu, J.; Ma, J.; Zhu, Q.; Zhang, Z.; Wu, C. and Han, B. Transformation of atmospheric CO₂ catalyzed by protic ionic liquids: efficient synthesis of 2-oxazolidinones. *Angew. Chem. Int. Ed.*, 2015, **54**, 5399-5403. (DOI: 10.1002/anie.201411969)

(7) Aresta, M. Carbon dioxide as chemical feedstock, 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

(8) Martín, C.; Fiorani, G. and Kleij, A. W. Recent advances in the catalytic preparation of cyclic organic carbonates. *ACS Catal.*, 2015, **5**, 1353-1370. (DOI: 10.1021/cs5018997)

- (9) Qui, J.; Zhao, Y.; Li, Z.; Wang, H.; Fan, M. and Wang, J. Efficient ionic-liquid-promoted chemical fixation of CO₂ into α -alkylidene cyclic carbonates. *ChemSusChem*, 2017, **10**, 1120-1127. (DOI:10.1002/cssc.201601129)
- (10) Jiang, X.; Gou, F.; Chen, F. and Jing, H. Cycloaddition of epoxides and CO₂ catalyzed by bisimidazole-functionalized porphyrin cobalt (III) complexes. *Green Chem.*, 2016, **18**, 3567-3576. (DOI: 10.1039/C6GC00370B)
- (11) Scrosati, B.; Hassoun, J. and Sun, Y.-K. Lithium-ion batteries, a look into the future. *Energy Environ. Sci.*, 2011, **4**, 3287-3292. (DOI: 10.1039/c1ee01388b)
- (12) Crowther, O.; Keeny, D.; Moureau, D. M.; Meyer, B.; Salomon, M. and Hendrickson, M. Electrolyte optimization for the primary lithium metal air battery using an oxygen selective membrane. *J. Power Sources*, 2012, **202**, 347-351. (DOI:10.1016/j.jpowsour.2011.11.024)
- (13) Clements, J. H. Reactive Applications of cyclic alkylene carbonates. *Ind. Eng. Chem. Res.*, 2003, **42**, 663-674. (DOI: 10.1021/ie020678i)
- (14) Besse, V.; Camara, F.; Voirin, C.; Auvergne, R.; Caillol, S. and Boutevin, B. Synthesis and application of unsaturated cyclocarbonates. *Polym. Chem.*, 2013, **4**, 4545-4561. (DOI:10.1039/C3PY00343D)
- (15) Kayaki, Y.; Yamamoto, M. and Ikariya, T. N-Heterocyclic carbenes as efficient organocatalysts for CO₂ fixation reactions. *Angew. Chem. Int. Ed.*, 2009, **48**, 4194-4197. (DOI: 10.1002/anie.200901399)
- (16) Desens, W. and Werner, T. Convergent activation concept for CO₂ fixation in carbonates. *Adv. Synth. Catal.*, 2016, **358**, 622-630. (DOI: 10.1002/adsc.201500941)

- (17) Stewart, J. A.; Drexel, R.; Arstad, B.; Reubsaet, E.; Weckhuysen, B. M. and Bruijninx, P. C. A. Homogeneous and heterogenised masked N-heterocyclic carbenes for bio-based cyclic carbonate synthesis. *Green Chem.*, 2016, **18**, 1605-1618. (DOI: 10.1039/c5gc02046h)
- (18) Jing, H.; Nguyen, S. T. SnCl₄-organic base: Highly efficient catalyst system for coupling reaction of CO₂ and epoxides. *J. Mol. Catal. A: Chem.*, 2007, 261, 12-15. (DOI:10.1016/j.molcata.2006.07.057)
- (19) Jin, L.; Jing, H.; Chang, T.; Bu, X.; Wang, L.; Liu, Z. Metal porphyrin/phenyltrimethylammonium tribromide: High efficient catalysts for coupling reaction of CO₂ and epoxides. *J. Mol. Catal. A-Chem.*, 2007, **261**, 262-266. (DOI:10.1016/j.molcata.2006.06.011)
- (20) Castro-Osma, J. A.; Lamb, K. J.; North, M. Cr(salophen) complex catalyzed cyclic carbonate synthesis at ambient temperature and pressure. *ACS Catal.* 2016, **6**, 5012-5025. (DOI: 10.1021/acscatal.6b01386)
- (21) Gao, P.; Zhao Z.; Chen, L.; Yuan, D. and Yao, Y. Dinuclear aluminum poly(phenolate) complexes as efficient catalysts for cyclic carbonate synthesis. *Organometallics*, 2016, **35**, 1707-1712. (DOI: 10.1021/acs.organomet.6b00153)
- (22) Peña-López, M.; Neumann, H. and Beller, M. Iron-catalyzed synthesis of five-membered cyclic carbonates from vicinal diols: urea as sustainable carbonylation agent. *Eur. J. Org. Chem.*, 2016, 3721-3727. (DOI: 10.1002/ejoc.201600476)
- (23) Stewart, J. A.; Drexel, R.; Arstad, B.; Reubsaet, E.; Weckhuysen, B. M. and Bruijninx, P. C. A. Homogeneous and heterogenised masked N-heterocyclic carbenes for bio-based cyclic carbonate synthesis. *Green Chem.*, 2016, **18**, 1605-1618. (DOI: 10.1039/c5gc02046h)

- (24) Kurteva, V. B. and Afonso, C. A. M. A study on the intramolecular catalytic aldol cyclodehydration of 3,4-disubstituted 1,6-dialdehydes. *J. Mol. Catal. A: Chem.*, 2005, **234**, 159-167. (DOI:10.1016/j.molcata.2005.02.028)
- (25) Itaya, T.; Iida, T.; Natsutani, I. and Ohba, M. Reactions of oxalyl chloride with 1,2-cycloalkanediols in the presence of triethylamine. *Chem. Pharm. Bull.*, 2002, **50**, 83-86.
- (26) Davies, A. G.; Hua-De, P. and Hawari, J. A. A. The reaction of 1,3,2-dioxastannolanes with diacyl chlorides: decarbonylation in the reaction with oxalyl chloride. *J. Organomet. Chem.*, 1983, **256**, 251-260. (DOI:10.1016/S0022-328X(00)99202-7)
- (27) Chavan, S. P. and Bhanage, B. M. Pd/C: an efficient and heterogeneous protocol for oxidative carbonylation of diols to cyclic carbonate. *Tetrahedron Lett.*, 2014, **55**, 1199-1202. (DOI:10.1016/j.tetlet.2013.12.116)
- (28) (a) Bobbink, F. D.; Gruszka, W.; Hulla, M.; Das, S. and Dyson, P. J. Synthesis of cyclic carbonates from diols and CO₂ catalyzed by carbenes. *Chem. Commun.*, 2016, **52**, 10787-10790. (DOI:10.1039/C6CC05730F)
- (29) Jin, L.; Lei, Y.; Goodrich, P.; Gunaratne, H. Q. N. and Seddon, K. R. *Unpublished work, manuscript in preparation.*
- (30) Reithofer, M. R.; Sum, Y. N. and Zhang, Y. Synthesis of cyclic carbonates with carbon dioxide and cesium carbonate. *Green Chem.*, 2013, **15**, 2086-2090. (DOI:10.1039/C3GC40790J)
- (31) Babu, R.; Roshan, R.; Kathalikkattil, A. C.; Kim, D. W. and Park, D. W. Rapid, microwave-assisted synthesis of cubic, three-dimensional, highly porous MOF-205 for room

temperature CO₂ fixation via cyclic carbonate synthesis. *ACS Appl. Mater. Interfaces*, 2016, **8**, 33723-33731. (DOI: 10.1021/acsami.6b12458)

(32) Guo, X.; Zhou, Z.; Chen, C.; Bai, J.; He, C. and Duan, C. New rht-type metal-organic frameworks decorated with acylamide groups for efficient carbon dioxide capture and chemical fixation from raw power plant flue gas. *ACS Appl. Mater. Interfaces*, 2016, **8**, 31746-31756. (DOI: 10.1021/acsami.6b13928)

(33) Zhou, H.; Wang, G. X.; Zhang, W. Z. and Lu, X. B. CO₂ adducts of phosphorus yields: Highly active organocatalysts for carbon dioxide transformation. *ACS Catal.*, 2015, **5**, 6773-6779. (DOI: 10.1021/acscatal.5b01409)

(34) Freemantle, M. *An Introduction to Ionic Liquids*, 2010 Royal Society of Chemistry, Cambridge.

(35) Wasserscheid, P. and Welton, T. *Ionic Liquids in Synthesis*, 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

(36) Liu, S.; Suematsu, N.; Maruoka, K. and Shirakawa, S. Design of bifunctional quaternary phosphonium salt catalysts for CO₂ fixation reaction with epoxides under mild conditions. *Green Chem.*, 2016, **18**, 4611-4615. (DOI:10.1039/C6GC01630H)

(37) Kim, D.; Moon, Y.; Ji, D.; Kim, H. and Cho, D. Metal-containing ionic liquids as synergistic catalysts for the cycloaddition of CO₂: A density functional theory and response surface methodology corroborated study. *ACS Sustainable Chem. Eng.*, 2016, **4**, 4591-4600. (DOI: 10.1021/acssuschemeng.6b00711)

(38) Liu, M.; Liang, L.; Li, X.; Gao, X. and Sun, J. Novel urea derivative-based ionic liquids with dual-functions: CO₂ capture and conversion under metal- and solvent-free conditions. *Green Chem.*, 2016, **18**, 2851-2863. (DOI: 10.1039/C5GC02605A)

(39) Liu, M.; Li, X.; Liang L. and Sun, J. Protonated triethanolamine as multi-hydrogen bond donors catalyst for efficient cycloaddition of CO₂ to epoxides under mild and cocatalyst-free conditions. *J. CO₂ Util.*, 2016, **16**, 384-390. (DOI:10.1016/j.jcou.2016.10.004)

(40) Wu, S.; Wang, B.; Zhang, Y.; Elageed, E. H. M. and Wu, H. Phenolic hydroxyl-functionalized imidazolium ionic liquids: Highly efficient catalysts for the fixation of CO₂ to cyclic carbonates. *J. Mol. Catal. A: Chem.*, 2016, **418-419**, 1-8. (DOI:10.1016/j.molcata.2016.03.002)

(41) Tharun, J.; Bhin, K.-M.; Roshan, R.; Kim, D. W.; Kathalikkattil, A. C.; Babu, R.; Ahn, H. Y.; Won, Y. S. and Park, D.-W. Ionic liquid tethered post functionalized ZIF-90 framework for the cycloaddition of propylene oxide and CO₂. *Green Chem.*, 2016, **18**, 2479-2487. (DOI: 10.1039/C5GC02153G)

(42) Sadeghzadeh, S. M. A heteropolyacid-based ionic liquid immobilized onto fibrous nano-silica as an efficient catalyst for the synthesis of cyclic carbonate from carbon dioxide and epoxides. *Green Chem.*, 2015, **17**, 3059-3066. (DOI:10.1039/C5GC00377F)

(43) Zhang, W.; Wang, Q.; Wu, H.; Wu, P. and He, M. A highly ordered mesoporous polymer supported imidazolium-based ionic liquid: an efficient catalyst for cycloaddition of CO₂ with epoxides to produce cyclic carbonates. *Green Chem.*, 2014, **16**, 4767-4774. (DOI:10.1039/C4GC01245C)

(44) Wang, X.; Zhou, Y.; Guo, Z.; Chen, G.; Li, J.; Shi, Y.; Liu, Y. and Wang, J. Heterogeneous conversion of CO₂ into cyclic carbonates at ambient pressure catalyzed by ionothermal-derived meso-macroporous hierarchical poly(ionic liquid)s. *Chem. Sci.*, 2015, **6**, 6916-6924. (DOI: 10.1039/C5SC02050F)

(45) Wang, W.; Li, C.; Yan, L.; Wang, Y.; Jiang, M. and Ding, Y. Ionic liquid/Zn-PPh₃ integrated porous organic polymers featuring multifunctional sites: Highly active heterogeneous catalyst for cooperative conversion of CO₂ to cyclic carbonates. *ACS Catal.*, 2016, **6**, 6091-6100. (DOI: 10.1021/acscatal.6b01142)

(46) Guo, Z.; Cai, X.; Xie, J.; Wang, X.; Zhou, Y. and Wang, J. Hydroxyl-exchanged nanoporous ionic copolymer toward low-temperature cycloaddition of atmospheric carbon dioxide into carbonates. *ACS Appl. Mater. Interfaces*, 2016, **8**, 12812-12821. (DOI: 10.1021/acsami.6b02461)

(47) Hollingsworth, N.; Taylor, S. F. R.; Galante, M. T.; Jacquemin, J.; Longo, C.; Holt, K. B.; de Leeuw, N. H. and Hardacre, C. Reduction of carbon dioxide to formate at low overpotential using a superbase ionic liquid. *Angew. Chem. Int. Ed.*, 2015, **54**, 14164-14168. (DOI: 10.1002/anie.201507629)

(48) Ishikawa, T. Superbases for organic synthesis. 2009 John Wiley & Sons, Ltd, Chichester.

(49) Leito, I.; Koppel, I. A.; Koppel, I.; Kaupmees, K.; Tshepelevitsh, S. and Saanme, J. Basicity Limits of neutral organic superbases. *Angew. Chem. Int. Ed.*, 2015, **54**, 9262-9265. (DOI: 10.1002/anie.201503345)

(50) Caubère P. Unimetal super bases. *Chem. Rev.*, 1993, **93**, 2317-2334. (DOI: 10.1021/cr00022a012)

(51) Wang, C.; Luo, X.; Luo, H.; Jiang, D. E.; Li, H. and Dai, S. Tuning the basicity of ionic liquids for equimolar CO₂ capture. *Angew. Chem. Int. Ed.*, 2011, **50**, 4918-4922. (DOI: 10.1002/anie.201008151)

(52) Xiong, D.; Cui, G.; Wang, J.; Wang, H.; Li, Z.; Yao, K. and Zhang, S. Reversible hydrophobic-hydrophilic transition of ionic liquids driven by carbon dioxide. *Angew. Chem. Int. Ed.*, 2015, **54**, 7265-7269. (DOI:10.1002/anie.201500695)

(53) Chen, K.; Shi, G.; Dao, R.; Mei, K.; Zhou, X.; Li, H. and Wang, C. Tuning the basicity of ionic liquids for efficient synthesis of alkylidene carbonates from CO₂ at atmospheric pressure. *Chem. Commun.*, 2016, **52**, 7830-7833. (DOI:10.1039/C6CC02853E)

(54) Zhao, Y.; Yang, Z.; Yu, B.; Zhang, H.; Xu, H.; Hao, L.; Han, B. and Liu, Z. Task-specific ionic liquid and CO₂-cocatalysed efficient hydration of propargylic alcohols to α -hydroxy ketones. *Chem. Sci.*, 2015, **6**, 2297-2301. (DOI: 10.1039/c5sc00040h)

(55) Zhao, Y. F.; Wu, Y. Y.; Yun, G. F.; Hao, L. D.; Gao, X.; Yang, Z. Z.; Yu, B.; Zhang, H. Y. and Liu, Z. M. Azole-anion-based aprotic ionic liquids: functional solvents for atmospheric CO₂ transformation into various heterocyclic compounds. *Chem. Asian J.*, 2016, **11**, 2735-2740. (DOI: 10.1002/asia.201600281)

(56) Taylor, S. F. R.; McCrellis, C.; McStay, C.; Jacquemin, J.; Hardacre, C.; Mercy, M.; Bell R. G. and de Leeuw, N. H. CO₂ capture in wet and dry superbase ionic liquids. *J. Solution Chem.* 2015, **4**, 511-527. (DOI:10.1007/s10953-015-0319-z)

(57) Tsuji, Y. and Ohno, H. Facile preparation of hydroxide ion or proton conductive ionic liquids by mixing tetra-n-butylphosphonium hydroxide and benzimidazole. *RSC Advances*, 2012, **2**, 11279-11284. (DOI: 10.1039/C2RA21482B)

(58) Tsuji, Y.; Mizumo, T. and Ohno, H. Simple synthesis of tetra-n-butylphosphonium benzimidazolate/benzimidazole mixture as a thermally stable proton conductor. *Chem. Commun.*, 2011, **47**, 3132-3134. (DOI: 10.1039/C0CC03170D)

(59) Hofmann, A. W. Beiträge zur Kenntniss der flüchtigen organischen basen. *Ann. Chem. Pharm.*, 1851, **78**, 253-286.

(60) Landini, D.; Maia, A. and Rampoldi, A. Stability of quaternary onium salts under phase-transfer conditions in the presence of aqueous alkaline solutions. *J. Org. Chem.*, 1986, **51**, 3187-3191. (DOI: 10.1021/jo00366a022)

(61) Clough, M. T.; Geyer, K.; Hunt, P. A.; Mertes, J. and Welton, T. Thermal decomposition of carboxylate ionic liquids: trends and mechanisms. *Phys. Chem. Chem. Phys.*, 2013, **15**, 20480-20495. (DOI: 10.1039/c3cp53648c)

(62) Bai, D.; Jing, H.; Liu, Q.; Zhu, Q.; Zhao X. Titanocene dichloride-Lewis base: An efficient catalytic system for coupling of epoxides and carbon dioxide. *Catal. Commun.* 2009, **11**, 155-157. (DOI:10.1016/j.catcom.2009.09.012)

(63) Liu, X.; Zhang, S.; Song, Q. W.; Liu, X.; Ma, R. and He, L. N. Cooperative calcium-based catalysis with 1, 8-diazabicyclo[5. 4. 0]-undec-7-ene for the cycloaddition of epoxides with CO₂ at atmospheric pressure. *Green Chem.*, 2016, **18**, 2871-2876. (DOI: 10.1039/C5GC02761F)

Sustainable cyclic carbonate production, utilising carbon dioxide and azolate ionic liquids

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The azolate ionic liquids exhibit superior recyclability and provide non-halide catalyst system for CO₂ conversion.

